
Molecular Symmetry and *Ab Initio* Calculations. II. Symmetry-Matrix and Symmetry-Supermatrix in the Dirac-Fock Method

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ABSTRACT

The concepts of symmetry-matrix and symmetry-supermatrix introduced in article I [*J. Comput. Chem.*, **10**, 957 (1989)] can be generalized to the Dirac-Fock method. By using the semidirect product decomposition of O_h and the linear vector space theory, the irreducible representation basis of O_h for any molecular system (O_h or its subgroups) can be deduced analytically in the nonorthonormal Cartesian Gaussian basis. This method is extended to discuss the double-valued representations of O_h^* in the complex Cartesian Gaussian spinor basis. In the double-valued irreducible representation basis of D_2^* , the matrix of kinetic operator $c\vec{\sigma} \cdot \vec{p}$ in the Dirac-Fock equation can be reduced into a real symmetric and can be grouped into classes under the operations in D_{3d} . Therefore, the symmetry-matrix and symmetry-supermatrix can also be used in the Dirac-Fock method to reduce the storage of two electron integrals and calculations of Fock matrix during iterations by a factor of ca. g^2 (g is the order of the molecular symmetry group). In addition, a method to deal with the nonorthonormal space is presented. © 1996 by John Wiley & Sons, Inc.

Introduction

In article I¹ the concepts of the symmetry-matrix and symmetry-supermatrix have been intro-

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duced and implemented into the restricted Hartree-Fock (HF) *ab initio* calculation program. By using symmetry-matrix and symmetry-supermatrix, the storage of two-electron integrals can be reduced by a factor of ca. g^2 (g is the order of the molecular symmetry group) and the calculation of the Fock matrix during iterations can be reduced

proportionally. In addition, the convergence behavior of highly symmetric molecules can be improved.

Until now, this method has not been implemented in some common programs, such as GAUSSIAN92, GAMESS,² and TURBOMOLE,³ in which only a factor of g can be gained by using symmetry. In this article we will further illustrate the concepts of symmetry-matrix and symmetry-supermatrix. The average symmetry-matrix will be introduced in order to simplify the operation rules of symmetry-matrix and symmetry-supermatrix.

The application of the symmetry-supermatrix is always combined with the average density symmetry-matrix. The density matrix of one component of the multidimensional irreducible representation (IR) is not totally symmetric, but after summation over all components within IR the density matrix can have a correct symmetry-matrix form only if every component has a correct phase. Obviously, these phases cannot be determined by the usual projection operator method.^{2,3} Therefore, we have developed a method to directly deduce the irreducible representation basis (IRB) of octahedral group in the Cartesian Gaussian basis. For some multidimensional IR, the components can be transformed under symmetry operations; thus these phases can be determined naturally. Therefore, only one component of the multidimensional IR is needed and allowed to form the average density symmetry-matrix of the IR.

In this article the concepts of symmetry-matrix and symmetry-supermatrix will be generalized to the Dirac-Fock method.

Symmetry-Matrix and Symmetry-Supermatrix

The use of molecular symmetry to reduce the storage and calculations in the *ab initio* calculations depends on the equivalence of the basis set.^{1,4-6}

Cartesian Gaussian functions

$$|I\rangle \equiv |l, m, n\rangle = x^l y^m z^n \exp(\alpha r^2);$$

$$l, m, n: \text{integer} \quad (1)$$

can be transformed mutually under the operation $\hat{R} \in O_h$. That is,

$$\hat{R}|I\rangle = \theta(I, I')|I'\rangle; \quad \theta(I, I') = \pm 1 \quad (2)$$

where $|I\rangle$ and $|I'\rangle$ are said to be equivalent. The

set of basis functions $\{|I\rangle: I = 1, 2, \dots, N\}$ can be grouped into classes, and any basis function in the class can be chosen as the class representative. The set of the class representatives

$$\{|\bar{i}\rangle \equiv |I_i\rangle: i = 1, 2, \dots, n\}$$

is called the average symmetry-set of basis functions, where n is the number of class representatives. The basis functions in the class can be transformed and added to the representative, and then the symmetry-set of basis functions can be defined as

$$\{|i\rangle \equiv n_i |I_i\rangle: i = 1, 2, \dots, n\}$$

where n_i is the number of basis functions in the i th class. For example, the set of basis functions for $L = l + m + n \leq 4$ can be grouped into a symmetry-set of basis functions

$$\{1, 3z, 3yz, 3z^2, xyz, 6yz^2, 3z^3, 3xyz^2, 3y^2z^2, 6yz^3, 3z^4\}$$

where the Gaussian function part of the basis function is omitted.

The spin-restricted HF equation for closed shell can be represented as

$$F(IJ) = h(IJ) + \sum_{K,L} P(IJ|KL) \cdot D(KL) \quad (3)$$

where $h(IJ)$ is the one-electron part of Fock matrix $F(IJ)$; $D(KL)$ is the density matrix; and $P(IJ|KL)$ is the supermatrix represented by two electron integrals⁷:

$$P(IJ|KL) = 2(IJ\|KL) - \frac{1}{2}[(IK\|JL) + (IL\|JK)]$$

Similarly, these matrices can be grouped into average symmetry-matrices. For example,

$$\bar{F}(i) = \{\bar{F}(i) \equiv F(I_i J_i): i = 1, 2, \dots, m\} \quad (4)$$

where m is the number of class representatives and $F(I_i J_i)$ is the representative in the i th class such that¹

$$\hat{R}F(IJ)\hat{R}^\dagger = \theta(IJ)F(I_i J_i) \quad (5)$$

where \hat{R} includes any symmetry operation which satisfies this equation [e.g., $F(IJ) = F(JI)$] and $\theta(IJ)$ is the sign of matrix element (IJ) different from the class representative:

$$\theta(IJ) = \theta(I, I_i)\theta(J, J_i) \quad (6)$$

If $\hat{R}F(IJ)\hat{R}^\dagger = -F(IJ)$, then $F(IJ) = 0$ and all elements in this class are equal to zero, so only nonzero representatives need to be calculated and stored. The symmetry-matrix is defined as

$$\mathbf{F}(i) = \{F(i) \equiv m_i F(I_i J_i) : i = 1, 2, \dots, m\} \quad (7)$$

where m_i is the number of matrix elements in the i th class. The overlap symmetry-matrix between basis functions for $L \leq 3$ can be represented as

$$\begin{aligned} &\{ \langle 1|1 \rangle, 6\langle 1|z^2 \rangle, 3\langle z|z \rangle, 12\langle y|yz^2 \rangle, 6\langle y^2|z^2 \rangle, \\ &3\langle yz|yz \rangle, 6\langle z|z^3 \rangle, 3\langle z^2|z^2 \rangle, 6\langle x^2 y|yz^2 \rangle, \\ &\langle xyz|xyz \rangle, 12\langle y^2 z|z^3 \rangle, 6\langle yz^2|yz^2 \rangle, 3\langle z^3|z^3 \rangle \} \end{aligned}$$

Thus 20×20 elements in the overlap matrix are now reduced to 13 elements in the overlap symmetry-matrix.

The symmetry-matrix is similar to the skeleton matrix in the reference⁶ except that the I is a shell in the latter case. The skeleton matrix is a reduced form and usually should be symmetrized to recover the correct matrix.^{2,8} In our case the transformation of matrix elements is simple [eq. (5)], so the matrix elements in the class can be added to class representatives to form the symmetry-matrix. By using the symmetry-matrix, the matrix represented by two subscripts (IJ) can be reduced to a vector represented by subscript i ; thus the trace of matrix multiplication can be reduced to the scalar product of vectors. For example,

$$\sum_{IJ}^{N^2} F(IJ) \cdot D(IJ) = \sum_i^m F(i) \bar{D}(i) \quad (8)$$

where $\bar{D}(i)$ is the average symmetry-matrix of the density

$$\bar{D}(i) = \sum_{IJ \in (i)}^{m_i} \frac{1}{m_i} \theta(IJ) D(IJ) \quad (9)$$

and

$$F(i) = \sum_{IJ \in (i)}^{m_i} \theta(IJ) F(IJ) \quad (10)$$

Substituting eqs. (9) and (10) into (8), eq. (8) can be proved since $\theta^2(IJ) = 1$ and $\sum_i^m m_i = N^2$. Therefore, eq. (3) can be reduced to

$$F(i) = h(i) + \sum_j P(i, j) \bar{D}(j) \quad (11)$$

where $P(i, j)$ is called the symmetry-supermatrix.

The transformation of two-electron integrals to $P(i, j)$ is carried out "on the fly" (i.e., as soon as the two-electron integral has been calculated). The contribution of two-electron integrals ($IJ \| KL$) to $P(i, j)$ can be written as

$$P(i, j) := P(i, j) + 2\theta(IJ)\theta(KL)(IJ \| KL);$$

$$(IJ) \in (i), (KL) \in (j) \quad (12a)$$

$$P(k, l) := P(k, l) - \frac{1}{2}\theta(IK)\theta(JL)(IJ \| KL);$$

$$(IK) \in (k), (JL) \in (l) \quad (12b)$$

$$P(m, n) := P(m, n) - \frac{1}{2}\theta(IL)\theta(JK)(IJ \| KL);$$

$$(IL) \in (m), (JK) \in (n) \quad (12c)$$

where the first equation represents the Coulomb interaction and the last two represent the exchange interaction. Since $P(i, j) = P(j, i)$, only $\frac{1}{2}m(m+1)$ elements of $P(i, j)$ need to be stored and the calculation of eq. (11) can be reduced correspondingly.

The symmetry-supermatrix defined in this article is not the symmetry unique two-electron integrals (i.e., a petite list of two-electron integrals in GAMESS² and TURBOMOLE³). They must be further reduced to form $P(i, j)$,¹ and thus the storage of $P(i, j)$ can be further reduced by a factor of ca. g in comparison with that of the petite list of two-electron integrals. However, the calculation of two-electron integrals can only be reduced by a factor of ca. g , and the concept of symmetry-supermatrix cannot be used in the usual direct self-consistent field method,^{2,3} where two-electron integrals are not saved and need to be recalculated during each iteration.

In this article we will extend the symmetry-matrix and symmetry-supermatrix to the Dirac-Fock method. The Dirac equation contains the electron spin operator, so the representations of the double-point group must be considered. The most important thing is to find the appropriate complex spinor basis which satisfies the relation of eq. (5).

The Cartesian Gaussian basis is nonorthonormal, and therefore the representations of the self-adjoint and unitary operators in the nonorthonormal space is discussed in the next section. We then use the linear vector space theory to find directly the irreducible representations and their direct product decompositions in the Cartesian Gaussian basis. Finally, representations of double-group O_h^* in the complex Cartesian Gaussian spinor basis in the Dirac-Fock method are discussed.

Nonorthonormal Space

In an n -dimensional space $V(n)$ spanned by a basis $\{|i\rangle: i = 1, 2, \dots, n\}$, a reciprocal (or dual) basis $\{|\bar{i}\rangle: i = 1, 2, \dots, n\}$ can be defined such that⁸

$$\langle \bar{i}|j\rangle = \delta_{ij} \equiv \begin{cases} 1, & i = j, \\ 0, & i \neq j \end{cases} \quad (13)$$

Theorem 1. *If*

$$|x\rangle = \sum_i |i\rangle x^i, \quad \forall x \in V(n) \quad (14)$$

then $x^i = \langle \bar{i}|x\rangle$.

Proof:

Multiplying by $\langle \bar{j}|$ on both sides of eq. (14) and using the orthonormal relation of eq. (13), we get

$$\langle \bar{j}|x\rangle = \langle \bar{j}|\sum_i |i\rangle x^i = x^j \quad \text{Q.E.D.}$$

Thus any vector $|x\rangle$ in $V(n)$ can be represented as

$$|x\rangle = \sum_i |i\rangle \langle \bar{i}|x\rangle \equiv |i\rangle x_i \quad (15)$$

where the subscript i appears twice, which means summation over i , and the summation sign is omitted. We will use this summation convention in this article.

Similarly, we can get

$$|x\rangle = |\bar{i}\rangle \langle i|x\rangle \equiv |\bar{i}\rangle x_i \quad (16)$$

In the nonorthonormal space every vector has two representations $\{x^i \equiv \langle \bar{i}|x\rangle\}$ and $\{x_i \equiv \langle i|x\rangle\}$, called contravariant and covariant, respectively. Therefore, two representations of the unit (identity) operator can be obtained from eqs. (15) and (16):

$$I = |i\rangle \langle \bar{i}|, \quad I = |\bar{i}\rangle \langle i| \quad (17)$$

If the overlap matrix $[\langle i|j\rangle]$ is known, two vector representations in the nonorthonormal space can be transformed using following equations:

$$\begin{aligned} \langle i|x\rangle &= \langle i|I|x\rangle \\ &= \sum_j \langle i|j\rangle \langle \bar{j}|x\rangle; \quad i = 1, \dots, n \end{aligned} \quad (18)$$

Multiplying by the unit operator on both sides of A , we get

$$I \cdot A \cdot I = |i\rangle \langle \bar{i}| A |j\rangle \langle \bar{j}| = A^{ij} |i\rangle \langle \bar{j}| \quad (19a)$$

$$I \cdot A \cdot I = |\bar{i}\rangle \langle i| A |j\rangle \langle \bar{j}| = A_{ij} |\bar{i}\rangle \langle \bar{j}| \quad (19b)$$

$$I \cdot A \cdot I = |i\rangle \langle \bar{i}| A |j\rangle \langle \bar{j}| = A_{ij}^i |i\rangle \langle \bar{j}| \quad (19c)$$

$$I \cdot A \cdot I = |\bar{i}\rangle \langle i| A |j\rangle \langle \bar{j}| = A_i^j |\bar{i}\rangle \langle \bar{j}| \quad (19d)$$

where subscript i and j appear twice, so summation over them is implied. There are four representations for each operator in a nonorthonormal space, which can be transformed using eq. (18). In eq. (3), the density matrix $D(IJ)$ is represented as eq. (19a), and the others are represented as eq. (19b).

The adjoint operator A^\dagger is defined as

$$\langle i|A^\dagger|j\rangle \equiv \langle A|i\rangle \langle \bar{j}| = \langle j|A|i\rangle^*; \quad \forall |i\rangle, |j\rangle \in V(n)$$

The representations of a self-adjoint operator ($A^\dagger = A$) only in eqs. (19a) and (19b) are Hermitian:

$$\langle i|A|j\rangle = \langle j|A|i\rangle^*; \quad \langle \bar{i}|A|\bar{j}\rangle = \langle \bar{j}|A|\bar{i}\rangle^*$$

The representations of a unitary operator ($U^\dagger = U^{-1}$) only in eqs. (19c) and (19d) are unitary:

$$\sum_j \langle \bar{i}|U^\dagger|j\rangle \langle \bar{j}|U|k\rangle = \delta_{ik}$$

In the nonorthonormal space the overlap matrix $|\bar{i}\rangle \langle i|j\rangle \langle \bar{j}|$ can be diagonalized, and its eigenvectors are orthogonal:

$$\sum_j \langle i|j\rangle \langle \bar{j}|O_a\rangle = \langle i|\tilde{O}_a\rangle s_a; \quad i, a = 1, \dots, n$$

where $\langle \bar{i}|O_a\rangle = \langle i|\tilde{O}_a\rangle$ and $\langle O_a|O_a\rangle = s_a$. Therefore, a unitary matrix ($[\langle \bar{i}|O_a\rangle]$ or $[\langle i|\tilde{O}_a\rangle]$) can be found to transform the nonorthonormal basis into the orthogonal basis (but not normalized), or vice versa:

$$|O_a\rangle = \sum_i |i\rangle \langle \bar{i}|O_a\rangle \quad (20a)$$

$$|\bar{i}\rangle = \sum_a |O_a\rangle \langle \tilde{O}_a|i\rangle \quad (20b)$$

The overlap operator commutes with the molecular symmetry group, so the eigenvectors $\{|O_a\rangle\}$ are also the irreducible representation basis (IRB) of the molecular symmetry group.

IRB of O_h in the Cartesian Gaussian Basis

According to the definition of the semidirect product,⁹ O_h can be represented as

$$O_h = D_2 \wedge C_3 \wedge C_{2d} \times C_i \quad (21)$$

where \wedge means that the semidirect product, the subgroups in its left part (i.e., D_2 and $D_2 \wedge C_3 = T$) are invariant subgroups, but the subgroups on its right part ($C_3 \wedge C_{2d} = D_3$ and C_{2d}) are not invariant; \times means direct product; and c_i is the space inversion.

D_2 consists of identity and three twofold rotation axes along x , y , and z axes:

$$D_2 = \{e, c_{2x}, c_{2y}, c_{2z}\}$$

There are four threefold axes, but we only choose the rotation through 120 degrees about $[111]$:

$$c_3: x, y, z \rightarrow y, z, x$$

Similarly, the twofold axis c_{2d} is chosen as

$$c_{2d}: x, y, z \rightarrow -y, -x, -z$$

According to the vector space theory,¹⁰ two self-adjoint or unitary operators A and B commute if and only if there exists a complete orthonormal common eigenvectors. Since D_2 is an invariant subgroup, we can use D_2 to divide the Cartesian Gaussian basis into four IRB functions: A, B_x, B_y, B_z (Table I), which can be identified by the eigenvalues of c_{2y} and c_{2z} .

These irreducible representations of D_2 can be further reduced by using subgroup $D_3 = C_3 \wedge C_{2d}$. The irreducible representations B_x, B_y , and B_z can

be transformed under c_3 operation:

$$c_3: B_x, B_y, B_z \rightarrow B_y, B_z, B_x$$

Thus they will form a three-dimensional irreducible representation (IR) T ($|T, x\rangle = B_x, |T, y\rangle = B_y, |T, z\rangle = B_z$), and only B_z needs to be considered. IR A of D_2 can be further reduced into one-dimensional A and two-dimensional E ($|E, 1\rangle, |E, 2\rangle$). We can use the eigenvalue of c_{2d} to further identify these IRs:

$$\begin{aligned} c_{2d}|A_1\rangle &= +|A_1\rangle; & c_{2d}|E, 2\rangle &= +|E, 2\rangle; \\ & & c_{2d}|T_2, z\rangle &= +|T_2, z\rangle \\ c_{2d}|A_2\rangle &= -|A_2\rangle; & c_{2d}|E, 1\rangle &= -|E, 1\rangle; \\ & & c_{2d}|T_1, z\rangle &= -|T_1, z\rangle \end{aligned}$$

Therefore, the IRs of O can be obtained. For example, the class $\{x^2, y^2, z^2\}$ in A can be reduced to

$$\begin{aligned} |A_1\rangle &= x^2 + y^2 + z^2; & |E, 1\rangle &= x^2 - y^2; \\ & & |E, 2\rangle &= x^2 + y^2 - 2z^2 \end{aligned}$$

The function z in B_z belongs to IRB $|T_1, z\rangle$, the function xy belongs to $|T_2, z\rangle$, and the class $\{zx^2, zy^2\}$ can be reduced to

$$|T_1, z\rangle = z(x^2 + y^2); \quad |T_2, z\rangle = z(x^2 - y^2)$$

If we only discuss the angular distribution, the functions $x^2 + y^2 + z^2$ and 1 are the same, so the function $x^2 + y^2 + z^2$ can be neglected and an orthogonal IRB in the Cartesian Gaussian basis can be obtained. The basis functions in $L = 3$ can be orthogonal to the basis functions in $L = 1$, so from z^3 and $z(x^2 + y^2)$, an IRB function

$$|T_1, z\rangle = z(x^2 + y^2 - \frac{2}{3}z^2)$$

being orthogonal to z can be formed.

TABLE I.
The IRB Functions of D_2 in the Cartesian Gaussian Basis.

IR Γ_a	eigenvalue		IRB functions ^a of D_2
	c_{2y}	c_{2z}	
A	+1	+1	$1, x^2, y^2, z^2, xyz, y^2z^2, z^2x^2, x^2y^2$
B_x	-1	-1	$x, yz, xy^2, xz^2, x^3, yzx^2, yz^3, y^3z$
B_y	+1	-1	$y, zx, yz^2, yx^2, y^3, zxy^2, zx^3, z^3x$
B_z	-1	+1	$z, xy, zx^2, zy^2, z^3, xyz^2, xy^3, x^3y$

^a Gaussian function part $(2\pi)^{-3/4} \exp(-\frac{1}{2}r^2)$ is omitted.

For O_h , we can use g, u to denote even and odd parity, respectively, under the space inversion. The orthonormal IRB of O_h in the Cartesian Gaussian basis is represented in Table II. These IRB functions are the common eigenvectors of c_{2y} , c_{2z} , and c_{2d} , and c_3 can be used to determine their degeneracies: A , E , or T . If we choose another c'_{2d} : $x, y, z \rightarrow -x, -z, -y$, then the IRB functions of IR E are

$$|E_g, 1\rangle = y^2 - z^2; \quad |E_g, 2\rangle = y^2 + x^2 - 2z^2$$

which are different from Table II, but the subspace spanned by them is the same.

For multidimensional irreducible representations (IRs), we only need to know one of the basis functions and the others can be obtained through symmetry operations (except for the two-dimensional IR E). The density matrix of one component of multidimensional IR is not totally symmetric, but after summation over all components within IR it may become totally symmetric only if every component of the IR has a correct phase. The

density matrix of IR Γ can be represented as

$$D_{pq}^\Gamma(IJ) = \sum_{a=1}^{d_\Gamma} \langle \tilde{a} | p\Gamma a \rangle \langle q\Gamma a | \tilde{j} \rangle \quad (22)$$

where p, q represent the different IRBs belonging to the same IR Γ ; a denotes the component of multidimensional IR; and d_Γ is the degeneracy of Γ . It can be transformed into the density symmetry-matrix

$$D_{pq}^\Gamma(i) = \sum_{(IJ) \in (i)} \theta(IJ) D_{pq}^\Gamma(IJ) \quad (23)$$

By using symmetry-matrix, the symmetry density matrix of one component also can be calculated and satisfies

$$\begin{aligned} D_{pq}^{\Gamma a}(i) &= \sum_{(IJ) \in (i)} \theta(IJ) \langle \tilde{a} | p\Gamma a \rangle \langle q\Gamma a | \tilde{j} \rangle \\ &= \frac{1}{d_\Gamma} D_{pq}^\Gamma(i) \end{aligned} \quad (24)$$

Therefore, we can use only one component to construct the multidimensional density matrix. The

TABLE II.
The Orthonormal IRB of O_h in Cartesian Gaussian Basis.

$ p\Gamma, a\rangle$	c_{2y}	c_{2z}	c_{2d}	IRB of O_h^a
$ 1A_{1g}\rangle$	1	1	1	1
$ 1T_{1u}, z\rangle$	-1	1	-1	z
$ 1E_g, 1\rangle$	1	1	-1	$\frac{1}{2}(x^2 - y^2)$
$ 1T_{2g}, z\rangle$	-1	1	-1	xy
$ 1A_{2u}\rangle$	1	1	-1	xyz
$ 2T_{1u}, z\rangle$	-1	1	-1	$\frac{1}{2}\sqrt{\frac{3}{5}}z(x^2 + y^2 - \frac{2}{3}z^2)$
$ 1T_{2u}, z\rangle$	-1	1	1	$\frac{1}{2}z(x^2 - y^2)$
$ 2A_{1g}\rangle$	1	1	1	$\frac{1}{3\sqrt{20}}(x^4 + y^4 + z^4 - 3(y^2z^2 + z^2x^2 + x^2y^2))$
$ 2E_g, 1\rangle$	1	1	-1	$\frac{1}{4\sqrt{21}}(x^2 - y^2)(x^2 + y^2 - 6z^2)$
$ 2T_{2g}, z\rangle$	-1	1	1	$\frac{1}{2\sqrt{21}}xy(x^2 + y^2 - 6z^2)$
$ 1T_{1g}, z\rangle$	-1	1	-1	$\frac{1}{2\sqrt{3}}xy(x^2 - y^2)$
$ 1E_u, 1\rangle$	1	1	-1	$\frac{1}{6}xyz(x^2 + y^2 - 2z^2)$
$ 2T_{2u}, z\rangle$	-1	1	1	$\frac{1}{12}z(x^2 - y^2)(x^2 + y^2 - 2z^2)$
$ 3T_{1u}, z\rangle$	-1	1	-1	$\frac{1}{8\sqrt{3}}z(x^4 + y^4 - 6x^2y^2)$
$ 4T_{1u}, z\rangle$	-1	1	-1	$\frac{1}{8\sqrt{30}}z^3(5x^2 + 5y^2 - z^2) - 15zx^2y^2$

Γ means irreducible representation; a : the components of IR Γ ; p : the different IRB belonging to the same IR Γ .

$|3T_{1u}, z\rangle, |4T_{1u}, z\rangle$ are not orthogonal.

^a Gaussian function part $(2\pi)^{-3/4} \exp(-\frac{1}{4}r^2)$ is omitted.

signs of these components $\{|p\Gamma a\rangle: a = 1, \dots, d_\Gamma, p = 1, \dots\}$, especially for IR E , must be chosen to satisfy eq. (24), and only in this case is eq. (22) totally symmetric.

Direct Products of O_h IR and Their Decomposition

The IRB functions of O_h can be used to describe atoms or the atomic orbitals in the O_h crystallized field. These functions also can be used to determine the molecular orbitals (i.e., the symmetry adapted linear combination of atomic orbitals, SALC).

Let us first consider the case in which all atomic orbitals are $s(L = 0)$ orbitals and the positions of equivalent atoms are

$$\{R_1, \dots, R_n\} \equiv \{\hat{R}R_1: \forall \hat{R} \in O_h\}$$

If R_1 is no symmetry (i.e., $R_1 = [a, b, c]$), we can get 48 equivalent atoms. If R_1 is located at some symmetry axis or plane, the number of equivalent atoms will be reduced. For example, $R_1 = [100]$, $n = 6$; $R_1 = [111]$, $n = 8$.

The s atomic orbital at R_a can be represented as

$$|s, R_a\rangle = \exp[-\alpha(r - R_a)^2]$$

and satisfies

$$R|s, R_a\rangle = |\hat{R}s, \hat{R}R_a\rangle = |s, \hat{R}R_a\rangle; \quad \forall R \in O_h$$

To get SALC, we defined the following functions on the group:

$$|X\rangle \equiv \sum_a^n |s, R_a\rangle \langle R_a|e_x\rangle \quad (25a)$$

$$|Y\rangle \equiv \sum_a^n |s, R_a\rangle \langle R_a|e_y\rangle \quad (25b)$$

$$|Z\rangle \equiv \sum_a^n |s, R_a\rangle \langle R_a|e_z\rangle \quad (25c)$$

where $\{|e_x\rangle, |e_y\rangle, |e_z\rangle\}$ is the Cartesian coordinate system and

$$\langle R_a|e_x\rangle = R_{ax}, \quad \langle R_a|e_y\rangle = R_{ay},$$

$$\langle R_a|e_z\rangle = R_{az}$$

It can be proved that the transformations of $|X\rangle, |Y\rangle, |Z\rangle$ are the same with x, y, z :

$$\hat{R}|X\rangle \equiv \sum_a^n |s, R_a\rangle \langle R_a|\hat{R}|e_x\rangle$$

$$\hat{R}x \equiv \hat{R}\langle r|e_x\rangle = \langle r|\hat{R}|e_x\rangle$$

Therefore, the SALC can be obtained only by replacing x, y, z , with X, Y, Z . The SALC of $R = [001]$ is shown in Table III. For example,

$$\begin{aligned} |E_g, 1\rangle &= \sum_a |s, R_a\rangle \langle R_a|X^2 - Y^2\rangle \\ &= |s, R_3\rangle + |s, R_4\rangle - |s, R_5\rangle - |s, R_6\rangle \end{aligned}$$

where $X^2 - Y^2$ is only defined on the positions of equivalent atoms, if $R_a = [100]$, $\langle R_a|X^2 - Y^2\rangle = 1$.

If the equivalent atom possesses s, p, d shells in which IRs are $a_{1g}, t_{1u}, e_g, t_{2g}$, then we must deal

TABLE III.
The SALC of $R_1 = [001]$ in O_h .

$ p\Gamma, a\rangle$	R_1	R_2	R_3	R_4	R_5	R_6	IRB functions
$ A_{1g}\rangle$	1	1	1	1	1	1	$ X^2 + Y^2 + Z^2\rangle$
$ E_g, 1\rangle$	0	0	1	1	-1	-1	$ X^2 - Y^2\rangle$
$ E_g, 2\rangle$	-2	-2	1	1	1	1	$ X^2 + Y^2 - 2Z^2\rangle$
$ T_{1u}, x\rangle$	0	0	1	-1	0	0	$ X\rangle$
$ T_{1u}, y\rangle$	0	0	0	0	1	-1	$ Y\rangle$
$ T_{1u}, z\rangle$	1	-1	0	0	0	0	$ Z\rangle$

with the direct products of representations. We use the uppercase to denote the interatomic representations and the lowercase the intraatomic representations. For A_6 ($R_1 = [001]$) molecule, we must discuss

$$\{A_{1g} \oplus E_g \oplus T_{1u}\} \otimes \{a_{1g} \oplus t_{1u} \oplus e_g \oplus t_{2g}\}$$

The basis of $T_{1u} \otimes t_{1u}$ is

$$\{Xx, Xy, Xz, Yx, Yy, Yz, Zx, Zy, Zz\}$$

By using D_2 , we get

$$A: Xx, Yy, Zz, \quad B_z: Xy, Yx$$

Then, using D_{3d} , we get

$$|A'_{1g}\rangle = Xx + Yy + Zz \quad (26a)$$

$$|E'_g, 1\rangle = Xx - Yy \quad (26b)$$

$$|T'_{1g}, z\rangle = Xy - Yx \quad (26c)$$

$$|T'_{2g}, z\rangle = Xy + Yx \quad (26d)$$

Thus

$$T_{1u} \otimes t_{1u} = A'_{1g} \oplus E'_g \oplus T'_{1g} \oplus T'_{2g} \quad (26)$$

Similarly, we can get

$$T_{1u} \otimes e_g = T'_{1u} \oplus T'_{2u} \quad (27)$$

where

$$|T'_{1u}, z\rangle = Z(x^2 + y^2 - 2z^2); \quad (27a)$$

$$|T'_{2u}, z\rangle = Z(x^2 - y^2) \quad (27b)$$

$$E_g \otimes e_g = A'_{1g} \oplus A'_{2g} \oplus E'_g \quad (28)$$

where

$$|A'_{1g}\rangle = 3(X^2 - Y^2)(x^2 - y^2) + (X^2 + Y^2 - 2Z^2)(x^2 + y^2 - 2z^2); \quad (28a)$$

$$|A'_{2g}\rangle = (X^2 - Y^2)(x^2 + y^2 - 2z^2) - (X^2 + Y^2 - 2Z^2)(x^2 - y^2); \quad (28b)$$

$$|E'_g, 1\rangle = (X^2 - Y^2)(x^2 + y^2 - 2z^2) + (X^2 + Y^2 - 2Z^2)(x^2 - y^2) \quad (28c)$$

Finally, the direct product of IR of A_6 containing up to d shell can be decomposed as follows:

$$\begin{aligned} &\{A_{1g} \oplus E_g \oplus T_{1u}\} \otimes \{a_{1g} \oplus t_{1u} \oplus e_g \oplus t_{2g}\} \\ &= 4A'_{1g} \oplus A'_{2g} \oplus A'_{1u} \oplus 5E'_g \oplus E'_u \\ &\quad \oplus 2T'_{1g} \oplus 3T'_{2g} \oplus 6T'_{1u} \oplus 3T'_{2u} \end{aligned} \quad (29)$$

The 6×10 dimensional representation space can be reduced into irreducible subspaces where the largest one is only six-dimensional.

By using similar methods, the IRB of A_8 , A_{12} , A_{24} , A_{48} also can be obtained.

Representations of Double-Point Group O_h^* in the Complex Cartesian Gaussian Spinor Basis

The Dirac equation of electrons in potential V can be written as

$$\hat{H}_D \Psi = \begin{pmatrix} V & c\vec{\sigma} \cdot \vec{p} \\ c\vec{\sigma} \cdot \vec{p} & V - 2c^2 \end{pmatrix} \begin{pmatrix} \psi_L \\ \psi_S \end{pmatrix} = E \begin{pmatrix} \psi_L \\ \psi_S \end{pmatrix} \quad (30)$$

where $\vec{\sigma}$ ($\sigma_x, \sigma_y, \sigma_z$) are the Pauli spin matrices; and ψ_L and ψ_S are the large and the small component of wave functions, respectively.

The Dirac-Fock method for atoms and molecules has been extensively considered.¹¹⁻¹⁸ The symmetry aspects of the construction of spinors for polyatomics have also been considered.¹⁹⁻²³ However, all these considerations are based on the atomic spinors,¹⁹ which are combined spherical harmonic with spin functions and usually not equivalent under the symmetry operations, so the concepts of symmetry-matrix and symmetry-supermatrix cannot be used.

We will use the complex Cartesian Gaussian spinor basis

$$j\phi_\sigma x^l y^m z^n \exp(-\alpha r^2); \quad j = 1, i; \sigma = \pm \frac{1}{2}; l, m, n = \text{integer} \quad (31)$$

where $j\phi_\sigma$ are spin functions; and $\phi_{\frac{1}{2}}$ and $i\phi_{\frac{1}{2}}$ are regarded as independent functions. Thus there are four spin basis functions: $\phi_{\frac{1}{2}}, i\phi_{\frac{1}{2}}, \phi_{-\frac{1}{2}}, i\phi_{-\frac{1}{2}}$ or represented as $\uparrow, i\uparrow, \downarrow, i\downarrow$. By using the basis of eq. (31), the $n \times n$ Hermitian matrix will be transformed into a $2n \times 2n$ real symmetric matrix, but the eigenvectors are at least doubly degenerate.

To solve the Dirac-Fock equation, it can be divided into two types, depending on whether the restricted kinetic balance or unrestricted kinetic balance is used.²⁴ In the restricted kinetic balance, the basis functions of the large component and small component are one-to-one correspondence:

$$\mu_S = \vec{\sigma} \cdot \vec{p} \mu_L$$

where μ_s and μ_L are the small and large component basis functions. Some computer codes¹⁵⁻¹⁸ belong to this type. In the unrestricted kinetic balance, the small component basis set satisfies

$$\{\mu_s\} \supset \{\vec{\sigma} \cdot \vec{p} \mu_L\}$$

Here $\{\mu_s\}$ is a Cartesian Gaussian spinor basis set, so the calculation of matrix elements is simpler. Some computer codes^{18,25} belong to the second type.

We follow the method implemented in the MOLFDIR program by Nieuwpoort et al.,²⁵ where the subgroup chain (C_{4h}^* and its subgroups) method will be extended to discuss the totally symmetric (O_h^*) Dirac-Fock Hamiltonian.

The kinetic operator $c\vec{\sigma} \cdot \vec{p}$ depends on spin, so diagonalizing this equation, we must use the double-valued representations of its symmetry group.

The double-valued representation is a projective representation. The phase factors can be absorbed into a basis, and then the projective representation can be reduced to a vector (single-valued) representation. To get the double-valued IRB in the complex Cartesian Gaussian spinor basis, the time reversal symmetry must be used. A similar method has been used to discuss the vibration of GaAs.²⁶

The twofold axes operated on the spin part can be represented as

$$\begin{aligned}\sigma_{2x} &= -i\sigma_x = \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}; \\ \sigma_{2y} &= -i\sigma_y = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}; \\ \sigma_{2z} &= -i\sigma_z = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}\end{aligned}$$

The time reversal with spin is

$$T = -i\sigma_y K$$

where K is the complex conjugate. Since $T\sigma_{2a} = -\sigma_{2a}T$; $a = x, y, z$, there are totally eight linear independent symmetry operations in double group D_2^* , including the time reversal operation. We choose two of them which are diagonalized:

$$\begin{aligned}TC_2(y) &= K \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} c_{2y}; \\ C_2(z) &= \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} c_{2z}\end{aligned}\quad (32)$$

where $C_2(y)$, $C_2(z)$ are twofold axes operated on spin and space components.

By using the eigenvectors of these two operations, the complex Cartesian Gaussian spinor basis can be divided into four double-valued IRBs of D_2^* (Table IV). These basis vectors can be mutually transformed under the operations of D_2^* :

$$\begin{aligned}C_2(y)|\bar{E}, 1\rangle &= |\bar{E}, 2\rangle; \\ C_2(z)|\bar{E}, 1\rangle &= |\bar{E}, 3\rangle; \\ C_2(x)|\bar{E}, 1\rangle &= |\bar{E}, 4\rangle\end{aligned}$$

Therefore, they form a four-dimensional representation which is equivalent to a Kramers doublet if the complex number is used, and then only two components $|\bar{E}, 1\rangle$ and $|\bar{E}, 2\rangle$ in \bar{E} representation (Table IV) are linear independent. We can only discuss the matrix of $\vec{\sigma} \cdot \vec{p}$ within the basis $|\bar{E}, 1\rangle$. By using these basis vectors, these matrix elements are real and can be transformed under operations of D_{3d} .

Let us consider the diagonalized operation

$$e^{-i(\pi/4)T} \cdot C_2(d) = K \begin{pmatrix} 1 & 0 \\ 0 & i \end{pmatrix} c_{2d}\quad (33)$$

which can be used to determine the IRB of O_h^* . Under consideration of spin functions, the single-valued IR A and E will be transformed into

TABLE IV.
The Double-Valued IRB of D_2^* in the Complex Cartesian Gaussian Spinor Basis.

$ \bar{\Gamma}, a\rangle$	$TC_2(y)$	$C_2(z)$	Double valued IRB of D_2^*
$ \bar{E}, 1\rangle$	-1	-i	$\uparrow A, -i \downarrow B_x, \downarrow B_y, -i \uparrow B_z$
$ \bar{E}, 2\rangle = C_2(y) \bar{E}, 1\rangle$	-1	i	$\downarrow A, -i \uparrow B_x, -\uparrow B_y, i \downarrow B_z$
$ \bar{E}, 3\rangle = C_2(z) \bar{E}, 1\rangle$	1	-i	$-i \uparrow A, -\downarrow B_x, -i \downarrow B_y, -\uparrow B_z$
$ \bar{E}, 4\rangle = C_2(x) \bar{E}, 1\rangle$	1	i	$-i \downarrow A, -\uparrow B_x, i \uparrow B_y, \downarrow B_z$

two-dimensional \bar{E} and four-dimensional \bar{G} (or \bar{U}), and three-dimensional T will split into \bar{E} and \bar{G} . According to the eigenvectors of eq. (33), the eigenvalues of IRs \bar{E}_1 , \bar{E}_2 , and \bar{G} are $(1, i)$, $(-1, -i)$ and $(-1, -i, 1, i)$, respectively. The double-valued IRBs with $L \leq 4$ are presented in the Table V.

For molecules with O_h , the number of equivalent atoms can be 6, 8, 12, 24, and 48. For A_6 , the interatomic IR of D_2 can be represented as X, Y, Z, X^2, Y^2, Z^2 . For the other cases, these equivalent atoms are first divided into classes by using the D_2 group and then transformed into IRs:

$$I_i, \quad X_i(\text{or } Y_i Z_i), \quad Y_i(\text{or } Z_i X_i), \quad Z_i(\text{or } X_i Y_i):$$

$$i = 1, \dots, a; a = 2, 3, 6, 12$$

If the atom possesses IRs a, b_x, b_y, b_z , then the direct product $(I_i \oplus X_i \oplus Y_i \oplus Z_i) \otimes (a \oplus b_x \oplus b_y \oplus b_z)$ can be decomposed as follows:

$$A: I_i a, X_i b_x, Y_i b_y, Z_i b_z$$

$$B_x: I_i b_x, X_i a, Y_i b_z, Z_i b_y$$

$$B_y: I_i b_y, X_i b_z, Y_i a, Z_i b_x$$

$$B_z: I_i b_z, X_i b_y, Y_i b_x, Z_i a$$

To get the component $\{|\bar{E}, 1\rangle\}$ of the double-valued IRB of D_2^* , we can also use the following projectors:

$$\begin{aligned} \uparrow P_A &= \frac{1}{2} \uparrow (I + c_{2x} + c_{2y} + c_{2z}) \\ -i \downarrow P_x &= -\frac{1}{2} i \downarrow (I + c_{2x} - c_{2y} - c_{2z}) \\ \downarrow P_y &= \frac{1}{2} \downarrow (I - c_{2x} + c_{2y} - c_{2z}) \\ -i \uparrow P_z &= -\frac{1}{2} i \uparrow (I - c_{2x} - c_{2y} + c_{2z}) \end{aligned}$$

where I is the unit operation; and c_{2x}, c_{2y}, c_{2z} are twofold axes along x, y, z .

By using the basis functions in $\{|\bar{E}, 1\rangle\}$ (Table IV), the matrix of $\vec{\sigma} \cdot \vec{p}$'s real symmetric and can be grouped into classes by using D_{3d} . In programming, we first calculate the matrices of $\nabla_x, \nabla_y, \nabla_z$, between the Cartesian Gaussian basis under O_h , and then transform them into double-valued IRBs of D_2^* .

Similarly, the supermatrix of the exchange operator between large and small components also can be calculated: The two-electron integrals ($I_L J_L \| K_S L_S$) are first calculated and then transformed into IRBs of D_2^* ; they are finally trans-

TABLE V.
The Double-Valued IRB of O_h^* in Complex Cartesian Gaussian Spinor Basis.

$ p\Gamma, a\rangle$	$ \bar{p}\bar{\Gamma}, a\rangle$	Double valued IRB of O_h^{*a}
$ 1A_{1g}\rangle$	$ 1\bar{E}_{1g}, 1\rangle$	\uparrow
$ 1T_{1u}, z\rangle$	$ 1\bar{E}_{1u}, 1\rangle$	$-i \downarrow x + \downarrow y - i \uparrow z$
$ 1T_{1u}, z\rangle$	$ 1\bar{G}_u, 1\rangle$	$-i \downarrow x - \downarrow y$
$ 1E_g, 1\rangle$	$ 1\bar{G}_g, 1\rangle$	$\uparrow (x^2 - y^2)$
$ 1T_{2g}, z\rangle$	$ 1\bar{E}_{2g}, 1\rangle$	$-i \downarrow yz + \downarrow zx - i \uparrow xy$
	$ 2\bar{G}_g, 1\rangle$	$-i \downarrow yz + \downarrow zx + 2i \uparrow xy$
$ 1A_{2u}\rangle$	$ 1\bar{E}_{2u}, 1\rangle$	$\uparrow xyz$
$ 2T_{1u}, z\rangle$	$ 2\bar{E}_{1u}, 1\rangle$	$-i \downarrow x(y^2 + z^2 - \frac{2}{3}x^2) + \downarrow y(z^2 + x^2 - \frac{2}{3}y^2) - i \uparrow z(x^2 + y^2 - \frac{2}{3}z^2)$
	$ 2\bar{G}_u, 1\rangle$	$-i \downarrow x(y^2 + z^2 - \frac{2}{3}x^2) - \downarrow y(z^2 + x^2 - \frac{2}{3}y^2)$
$ 1T_{2u}, 3\rangle$	$ 2\bar{E}_{2u}, 1\rangle$	$-i \downarrow x(y^2 - z^2) + \downarrow y(z^2 - x^2) - i \uparrow z(x^2 - y^2)$
	$ 3\bar{G}_u, 1\rangle$	$-i \downarrow x(y^2 - z^2) + \downarrow y(z^2 - x^2) + 2i \uparrow z(x^2 - y^2)$
$ 2A_{1g}\rangle$	$ 2\bar{E}_{1g}, 1\rangle$	$\uparrow [x^4 + y^4 + z^4 - 3(y^2 z^2 + z^2 x^2 + x^2 y^2)]$
$ 2E_g, 1\rangle$	$ 3\bar{G}_g, 1\rangle$	$\uparrow (x^2 - y^2)(x^2 + y^2 - 6z^2)$
$ 2T_{2g}, z\rangle$	$ 2\bar{E}_{2g}, 1\rangle$	$-i \downarrow yz(y^2 + z^2 - 6x^2) + \downarrow zx(x^2 + y^2 - 6y^2) - i \uparrow xy(x^2 + y^2 - 6z^2)$
	$ 4\bar{G}_g, 1\rangle$	$-i \downarrow yz(y^2 + z^2 - 6x^2) + \downarrow zx(x^2 + y^2 - 6y^2) + 2i \uparrow xy(x^2 + y^2 - 6z^2)$
$ 1T_{1g}, z\rangle$	$ 3\bar{E}_{1g}, 1\rangle$	$-i \downarrow yz(y^2 - z^2) + \downarrow zx(z^2 - x^2) - i \uparrow xy(x^2 - y^2)$
	$ 5\bar{G}_g, 1\rangle$	$-i \downarrow yz(y^2 - z^2) - \downarrow zx(z^2 - x^2)$

^a Gaussian function part $(2\pi)^{-3/4} \exp(-\frac{1}{4}r^2)$ is omitted.

formed into the symmetry-supermatrix of the exchange operator between large and small components.

Discussion and Conclusions

1. The octahedral group can be decomposed into serial semidirect products of Abelian subgroups, and then IRB of O_h can be easily obtained by using these subgroups. This method is much simpler than the projection operator method and the method of complete set of commuting operators (CSCO).^{27,28} By means of the symmetry-matrix,¹ only one component in the multidimensional IR is needed and allowed to construct the symmetry-matrix, so the storage and calculations can be reduced significantly.
2. The main reduction of storage and calculations comes from the equivalence of the basis. These highly equivalent bases are often nonorthogonal. By introducing the definition of the reciprocal (dual) basis, two representations of the unit (identity) operator can be established, and then two representations of vectors, four representations of operators, and transformation between these representations can be obtained. This method can be used to deal with the nonorthonormal space.
3. Based on the equivalence of basis, the symmetry-matrix and the symmetry-supermatrix can be used to reduce the storage of two-electron integrals and calculations of the Fock matrix during iterations (including electron correlation calculations in which the symmetry is conserved) by a factor of ca. g^2 (g is the order of the molecular symmetry group).
4. The symmetry operations in the matrix equivalent relation of eq. (5) can contain any kind of symmetry operations. For the nuclear attraction matrix and overlap matrix, many additional permutation operations can exist. For example,

$$\begin{aligned}\langle 1 | \frac{Z}{r} | x^2 y^2 \rangle &= \langle x | \frac{Z}{r} | x y^2 \rangle = \langle x^2 | \frac{Z}{r} | y^2 \rangle \\ &= \langle x y | \frac{Z}{r} | x y \rangle = \dots\end{aligned}$$

Thus the symmetry-matrix elements of the nuclear attraction can be further reduced by a factor of g_t ($g_t = m/m'$, where m' is the

number of the reduced symmetry-matrix elements by the additional symmetry operations). Therefore, the storage of the symmetry-supermatrix (two-electron integrals) can be further reduced by a factor of g_t^2 . The additional calculation needed is only to transform the average density symmetry-matrix into a new reduced symmetry-matrix form by using eq. (9). If the well-tempered, even-tempered,²⁹ or universal³⁰ basis sets in which the exponents are shared over s, p, d, f are used, a big additional saving for storage and calculation can be obtained.

5. Equivalence is closely related with symmetry. The equivalence relation of eqs. (2) and (5) can exist not only for these molecules with O_h or its subgroups, but also for molecules with any symmetry if an appropriate intrinsic coordinate system is established. We will extend these methods to discuss the molecules with I_h . In this case, the factor of reduction can reach 10^4 .
6. By using the double-valued IRB of D_2^* in the complex Cartesian Gaussian spinor basis, the matrices of $\vec{\sigma} \cdot \vec{p}$ and the exchange operator between large and small components can be transformed into real symmetric and can be grouped into classes by using D_{3d} . Therefore, the symmetry-matrix and symmetry-supermatrix can also be used in the Dirac-Fock method. The other parts of the Dirac-Fock matrix do not depend on spin, so the calculations of symmetry-matrix and symmetry-supermatrix are the same with that of the nonrelativistic case. After the formation of the Fock and the overlap symmetry-matrices, the IRB of O_h^* is used to diagonalize them into blocks.
7. In the Dirac-Fock method, in order to reduce the Fock matrix into real symmetric, the molecule must possess D_2^* or C_{2v}^* ; then the symmetry-matrix and the symmetry-supermatrix can be formed and used. D_2^* and C_{2v}^* are non-Abelian and can form a four-dimensional IRB in the complex Cartesian Gaussian spinor basis. The IRB functions of C_{2v}^* and C_{2v}^* are presented in Tables VI and VII, respectively. We can find that the IRB of C_{2v}^* is very different from that of D_2^* . It is very important to choose the correct invariant subgroup of the molecule (e.g., C_{2v}^* for the heteronuclear diatomic molecule and D_2^* for the homonuclear diatomic molecule). These

TABLE VI.
The IRB Functions of C_{2v} in the Cartesian Gaussian Basis.

Γ_a	eigenvalue		IRB functions ^a of C_{2v}
	$c_{2y}c_i$	c_{2z}	
A'	+1	+1	$1, z, x^2, y^2, z^2, x^2z, y^2z, z^3$
B'_x	1	-1	$x, xz, x^3, xy^2, xz^2, x^3z, xy^2z, xz^3$
B'_y	-1	-1	$y, yz, yx^2, y^3, yz^2, x^2yz, y^3z, yz^3$
B'_{xy}	-1	+1	$xy, xyz, x^3y, xy^3, xyz^2, x^3yz, xy^3z, xyz^3$

^aGaussian function part $(2\pi)^{-3/4} \exp(-\frac{1}{4}r^2)$ is omitted.

TABLE VII.
The Double-Valued IRB of C_{2v}^* in the Complex Cartesian Gaussian Spinor Basis.

$ \bar{\Gamma}, a >$	$TC_2(y)c_i$	$C_2(z)$	Double valued IRB of C_{2v}^*
$ \bar{E}, 1 >$	-1	-i	$+ \uparrow A', -i \downarrow B'_y, + \downarrow B'_x, -i \uparrow B'_{xy}$
$ \bar{E}, 2 > = C_2(y)c_i \bar{E}, 1 >$	-1	i	$+ \downarrow A', -i \uparrow B'_y, - \uparrow B'_x, +i \downarrow B'_{xy}$
$ \bar{E}, 3 > = C_2(z) \bar{E}, 1 >$	1	-i	$-i \uparrow A', - \downarrow B'_y, -i \downarrow B'_x, - \uparrow B'_{xy}$
$ \bar{E}, 4 > = C_2(x)c_i \bar{E}, 1 >$	1	i	$-i \downarrow A', - \uparrow B'_y, +i \uparrow B'_x, + \downarrow B'_{xy}$

results are the same as that of Oreg and Malli¹⁹ if the basis functions are transformed into atomic spinors.

Finally, we discuss a relativistic atomic case. In the unrestricted kinetic balance condition,²⁴ the large component and small component bases are, respectively, chosen up to f and g shells. The numbers of the large component and small component symmetry-matrix (overlap or nuclear attraction) elements are, respectively, equal to 7 and 11, in which the permutation symmetry of matrix elements (e.g., $\langle z|z \rangle = \langle 1|z^2 \rangle$) is included. The numbers of corresponding symmetry-supermatrix elements are 28 and 66. These numbers can, respectively, reach 20^4 and 35^4 if symmetry is not used. By using double-valued IRBs of D_2^* , the number of $\vec{\sigma} \cdot \vec{p}$ symmetry-matrix elements equals 23. It can be reduced into 10 for the symmetry-matrix of exchange operator between large and small components; then the number of the symmetry-supermatrix of exchange operator between large and small components equals 55. Therefore, the storage of the supermatrix in the atomic case can be reduced greatly by using the concept of symmetry-supermatrix.

This method can be only used for the unrestricted kinetic balance condition. In the restricted kinetic balance condition, the spin part must be considered explicitly for any matrix between two small components. Moreover, the basis set should be chosen as completely as possible (e.g., the well-tempered, even-tempered,²⁹ or universal³⁰ basis sets), so the coupling between different atomic shells in the matrix can be neglected. Thus the two kinds of computer codes^{16,25} can get the same results.

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